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PATENT APPLICATION

FOR

DIRECT SYNTHESIS OF OXIDE NANOSTRUCTURES OF LOW-MELTING METALS

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DIRECT SYNTHESIS OF OXIDE NANOSTRUCTURES OF LOW-MELTING METALS

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BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to the field of providing a synthesis technique to produce bulk amounts of gallium oxide nanowires, micron scale tubes, and paintbrush-like structures synthesized by direct reaction of atomic oxygen and hydrogen radicals with molten gallium.

Description of the Prior Art

Nanostructures find unique applications in electronics, optoelectronics, and catalysis due to their high surface to volume ratio, enhanced material characteristics due to quantum confinement effects and the high fraction of chemically similar surface sites. Functionalization of these nanostructures can only be achieved and become useful through the synthesis of bulk quantities of defined structures with controlled composition, crystallinity and morphology. Gallium oxide is a wide-bandgap material and is of interest due to its interesting bulk properties such as conduction and luminescence. These properties make it a candidate for gas sensing, catalytic, and optoelectronic device applications. Nanostructures of gallium oxide will be of particular interest for these applications.

Gallium oxide nanowires have been synthesized using several techniques such as physical evaporation, arc discharge, and catalyst assisted methods. All of these techniques have been thought to proceed according to two primary mechanisms. The first mechanism involves carbothermal reduction of gallium oxide to produce gas phase gallium suboxide growth species. The second mechanism relies on transition metal catalyst or evaporated gallium clusters to provide the necessary template for size control of the resulting nanowires.

SUMMARY OF THE INVENTION

Low melting metals (for example, gallium) provide the solvent medium for bulk nucleation and growth of nanowires, thereby eliminating the need for transition metal clusters as growth templates. Large droplets (millimeter size) or thin gallium films are spread on substrates to initiate nucleation with densities greater than 10 11 /cm. The large number density of the resulting nanowires makes the technique suitable and interesting for large-scale production. The gas phase chemistry is used to manipulate the absolute size, composition, and crystallinity of the nanowires. The only requirement is that the materials of interest should have extremely low solubility and low wetting characteristics with respect to molten gallium. If the solute wets the molten metal then two-dimensional crystals (platelets) or three-dimensional crystals are more likely to result rather than one-dimensional crystals.

Molten gallium can be used as the growth medium with synthesis of both silicon and carbon nanowires. In the instant invention, bulk nucleation and growth of gallium oxide nanostructures are formed from molten gallium pools using a microwave oxygen plasma. This direct synthesis approach for producing oxide nanowires can be easily extended to other metals such as aluminum, indium, tin, and

zinc. In addition, the instant invention provides a means for the synthesis of unique geometrical structures of crystalline gallium oxide in the form of tubes and nanopaintbrushes. Several geometrical nanostructures have been produced including spheres, rods, tubes, and belts. Of course it is contemplated that other geometric structures known in the art can be formed as well.

The synthesis of nanopaintbrushes represents first of its kind for any inorganic solid.

The present invention provides a method for the bulk synthesis of highly crystalline β-gallium oxide nanowires using molten gallium and a microwave plasma based gas chemistry. Gallium oxide nanowires, 20-100 nm thick and tens to hundreds of microns long were synthesized and confirmed to be crystalline and devoid of any structural defects using transmission electron microscopy. Multiple nucleation and growth of gallium oxide nanowires were obtained with appropriate gas phase composition of hydrogen and oxygen. Direct use of gallium melts in plasma environments allowed bulk synthesis with high nucleation densities and also allowed template-free synthesis of nanostructures with unique geometries. This plasma-based technique allowed for synthesis at temperatures much lower than conventional methods. The gas phase chemistry allowed manipulation of the nanostructure composition, structure, and morphology. Demonstration of this technique with gallium oxide presents a new route for synthesis of nanostructures of other important metal oxides such as indium oxide, tin oxide, and zinc oxide. Synthesis of unique geometrical structures of crystalline gallium oxide in the form of tubes and nanopaintbrushes have been developed. Several geometrical models of nanostructures including spheres, rods, tubes and belts have been developed resulting in the synthesis of the nanopaintbrushes.

Furthermore, the bulk synthesis of highly crystalline beta-

gallium oxide tubes, nanowires, and unique one-dimensional structures in the form of nanopaintbrushes has been accomplished using molten gallium and microwave plasma containing a mixture of monoatomic oxygen and hydrogen. Results show that multiple nucleation and growth of gallium oxide nanostructures occur directly out of molten gallium upon exposure to appropriate composition of hydrogen and oxygen in the gas phase. From the data, it is possible to present a growth model for the observed morphologies in the one-dimensional structures. Oxygen from the vapor phase forms surface adsorbed species on the molten gallium surface. These oxygenated gallium species dissolve into molten gallium followed by phase segregation to create multiple nuclei on the surface. In the absence of hydrogen in the plasma, these nuclei aggregate to form a polycrystalline crust on the molten gallium surface. However hydrogen/oxygen chemistry enables nuclei segregation on the gallium surface, preventing the complete crust formation. These nuclei grow in one dimension upon basal attachment of the bulk growth species. The surface dynamics of nuclei on molten gallium, i.e., pattern formation, and the time of coalescence determine the morphology of the resulting structure. Thus, results show that the gas phase chemistry allows manipulation of the nanostructure composition, structure, and morphology.

Moreover, the results show the synthesis of gallium oxide nanowires that were 20-100 nm thick and tens to hundreds of microns long. Individual nanowires were characterized for crystallinity, composition, and contamination using high-resolution transmission electron microscopy (HRTEM) and energy dispersive x-ray spectroscopy (EDX) respectively. Demonstration of this technique with gallium oxide certainly presents a new route for synthesis of nanostructures of other important metal oxides such as indium oxide, tin oxide, and zinc oxide.

In summary the present invention provides a method of synthesizing bulk quantities of highly crystalline noncatalytic low

melting metals, comprising the steps of exposing molten noncatalytic low melting metals and microwave plasma containing a mixture of monoatomic oxygen and hydrogen to selected amounts of hydrogen and oxygen in the gas phase; and forming multiple nucleation and growth of noncatalytic low melting metal nanostructures directly therefrom creating highly crystalline metal oxide nanowires devoid of any structural defects having a range of from 20 to 100 nm thick and a range of up to a thousand microns long and more typically from 10 to several hundred microns long.

It is an object of the present invention to utilize the direct synthesis approach involving low-melting metals providing a technique for working at lower temperatures than those required for traditional catalyst-assisted and physical evaporation methods.

It is another object of the present intention to synthesize one-dimensional nanostructures for metal oxides applying the direct synthesis approach of the instant invention, where one would not need the creation of gas phase growth species.

It is another object of the present invention to provide a method of control over the morphology of the one-dimensional nanostructures due to manipulability of the gas phase chemistry alone.

It is another object of the present intention to control the plasma uniformity over molten metal surfaces in order to tune the resulting one-dimensional morphology.

Other objects, features, and advantages of the invention will be apparent with the following detailed description taken in conjunction with the accompanying drawings showing a preferred embodiment of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

A better understanding of the present invention will be had upon reference to the following description in conjunction with the accompanying drawings in which like numerals refer to like parts throughout the several views and wherein:

Figure 1 shows an image taken with a scanning electrom microscope of multiple sub-micron thick gallium oxide needles grown from a large gallium pool;

Figure 2 shows an image taken with a scanning election microscope of multiple sub-micron thick gallium oxide needles grown from a large gallium pool;

Figure 3 shows an image taken with a scanning election microscope of multiple sub-micron thick gallium oxide needles grown from a large gallium pool;

Figure 4 shows an image taken with a scanning electrom microscope of nanometer scale gallium oxide rods;

Figure 5 shows an image taken with a scanning election microscope of nanometer scale gallium oxide rods;

Figure 6 shows an image taken with a scanning election microscope of nanometer scale gallium oxide rods;

Figure 7 shows an image taken with a scanning election microscope of nanometer scale gallium oxide rods;

Figure 8 shows an image taken with a scanning electrom microscope nanoscale wires, with well faceted one-dimensional structures thicker than 5 μm;

Figure 9 shows an image taken with a scanning election microscope nanoscale wires, with well faceted one-dimensional structures thicker than 5 μm;

Figures 10 shows an image taken with a scanning election microscope nanoscale wires, with well faceted one-dimensional structures thicker than 5 μm;

Figure 11 shows a plot of intensity vs. degree taken with an X-ray diffractometer confirming the as synthesized sample to be monoclinic gallium oxide phase (a0- 12.23 Å, b0=3.04 Å, c0=5.8 Å, b=103.7°, C2/m);

Figure 12 shows an image taken with a scanning electrom microscope depicting nanostructures with paintbrush-like and tubular morphologies on the substrate stage around the substrate that was towards the edge of the dense plasma region having individual whiskers with tip diameters ranging from 10-100 nm;

Figure 13 shows an image taken with a scanning election microscope depicting nanostructures with paintbrush-like and tubular morphologies on the substrate stage around the substrate that was towards the edge of the dense plasma region having individual whiskers with tip diameters ranging from 10-100 nm;

Figure 14 shows an image taken with a scanning election microscope depicting nanostructures with paintbrush-like and tubular morphologies on the substrate stage around the substrate that was towards the edge of the dense plasma region having individual whiskers with tip diameters ranging from 10-100 nm;

Figure 15 shows an image taken with a scanning election microscope depicting nanostructures with paintbrush-like and tubular morphologies on the substrate stage around the substrate

that was towards the edge of the dense plasma region having individual whiskers with tip diameters ranging from 10-100 nm;

Figure 16 shows an image taken with a scanning election microscope depicting nanostructures with paintbrush-like and tubular morphologies on the substrate stage around the substrate that was towards the edge of the dense plasma region having individual whiskers with tip diameters ranging from 10-100 nm;

Figure 17 shows an image taken with a scanning election microscope depicting nanostructures with paintbrush-like and tubular morphologies on the substrate stage around the substrate that was towards the edge of the dense plasma region having individual whiskers with tip diameters ranging from 10-100 nm;

Figure 18 shows an images taken with a high resolution scanning electrom microscope (HRTEM)(200kV JEOL 2010F) of a 25 nm thick gallium oxide nanowire together with an insert showing the corresponding selected area electron diffraction pattern taken along the [001] zone axis;

Figure 19 shows an energy dispersive x-ray spectrum (EDX) taken from an individual nanowire, confirming the elemental composition to be gallium and oxygen; and

Figure 20 is a schematic showing multiple nucleation and growth of metal oxide nanostructures out of a molten metal pool upon exposure to appropriate composition of hydrogen and oxygen in the gas phase, whereby the gas phase chemistry allows manipulation f the nanostructure composition, structure, and morphology.

Figure 21 is a schematic showing multiple nucleation and growth of Gallium oxide nanostructures out of a molten Gallium metal pool upon exposure to appropriate composition of hydrogen and oxygen in the gas phase, whereby the gas phase chemistry allows

manipulation of the nanostructure composition, structure, and morphology.

Figure 22 shows a bulk syntheses illustrating a one dimensional gallium oxide with sub-micron thick and nanometer scale gallium oxide rods;

Figure 23 shows a transmission electron microscopy analysis of individual nanowires depicting a bright field TEM image of an individual gallium oxide nanowire about 100 nm thick; and

Figure 24 shows a gallium oxide 1-D structure illustrating a micron scale gallium oxide tubes grown out of a gallium pool.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention relates to a novel direct synthesis technique for oxide nanostructures of a variety of low-melting metals. This technique involves exposing pool of a molten metal to an environment of oxygen and hydrogen radicals at elevated temperatures. Thermodynamic calculations show that molten metals such as Ga, In, Al, Sn, and Zn spontaneously oxidize at very moderate oxygen partial pressure. The present invention provides a method to inhibit spontaneous nucleation and growth of the metal oxide crust on the molten metal surface.

As shown in the schematic shown in Figure 20, multiple nucleation and growth of metal oxide nanostructures occurs directly out of a molten metal pool upon exposure to appropriate composition of hydrogen and oxygen in the gas phase. Oxygen from the vapor phase forms surface adsorbed species on the molten metal surface. These oxygenated metal species dissolve into the bulk melt followed by phase segregation to create multiple nuclei on the surface. In the absence of hydrogen in the plasma, these nuclei aggregate to form a polycrystalline crust on the molten metal surface. However

hydrogen/oxygen chemistry enables nuclei segregation on the melt surface, preventing the complete crust formation. These nuclei grow in one dimension upon basal attachment of the bulk growth species. The dynamics of the pattern formation and the time of nuclei coalescence determine the morphology of the resulting structure. Thus, the gas phase chemistry allows manipulation of the nanostructure composition, structure, and morphology.

Synthesis was carried out in a microwave plasma reactor (ASTEX 5010) using $H_2CH_4O_2$ gas mixtures. Quartz, alumina, pyrolytic boron nitride, glassy carbon, polycrystalline diamond film, porous graphite, and sapphire substrates were covered with a thin film of molten gallium and were exposed to a microwave plasma containing a range of gas phase species. During the plasma exposure, molten gallium flowed on all the substrates forming a thin film, which followed by formation of a thin polycrystalline film along with sparse nanowires. Gallium droplets were intentionally put on these polycrystalline oxide covered substrates and further synthesis experiments were carried out. The nanowires and other one-dimensional structures were grown from these large gallium drops. The substrate temperature was measured using an infrared pyrometer to be approximately 550°C for 700 W microwave power, 40 Torr total pressure, and 8.0 sccm O_2 in 100 sccm of hydrogen in the inlet stream. The experiments were performed at the following range of growth conditions: microwave power of 600-1200W, pressure of 30-60 Torr, growth duration of 1-12 hours, 0.6-10 sccm O_2 0-2 sccm CH_4 in 100 sccm of hydrogen in the feed gas. The post-synthesis samples were imaged using a LEO 1430 scanning electron microscope (SEM). As-grown samples were analyzed for crystalline quality using a Rigaku powder X-ray diffractometer (XRD). Individual nanowires were analyzed for crystallinity and composition using high-resolution transmission electron microscopy (HRTEM) (200kV JEOL 2010F) and Energy Dispersive X-ray spectroscopy (EDX). The samples for TEM analysis were prepared by scraping the nanowire mass from the

substrate, dispersing in acetone and dropping on to a copper TEM grid.

The feasibility of this direct synthesis approach has been demonstrate for Ga/Ga_2O_3. Also bulk amounts of highly crystalline beta-gallium oxide tubes, nanowires, and unique one-dimensional structures has been synthesized in the form of nanopaintbrushes using molten gallium and microwave plasma containing a mixture of monoatomic oxygen and hydrogen. Synthesis was carried out in a microwave plasma reactor (ASTEX 5010) using $H_2/CH_4/O_2$ gas mixtures. Quartz, alumina, pyrolytic boron nitride, glassy carbon, polycrystalline diamond film, porous graphite, and sapphire substrates were covered with a thin film of molten gallium and were exposed to a microwave plasma containing a range of gas phase species. The substrate temperature was measured using an infrared pyrometer to be approximately 550°C for 700 W microwave power, 40 Torr total pressure, and 8.0 sccm O2 in 100 sccm of hydrogen in the inlet stream. The experiments were performed at the following range of growth conditions: microwave power of 600-1200W, pressure of 30-60 Torr, growth duration of 1-12 hours, 0.6-10 sccm O_2 0-2 sccm CH_4 in 100 sccm of hydrogen in the feed gas.

Synthesis was carried out in a microwave plasma reactor (ASTEX 5010) using $H_2/CH_4/O_2$ gas mixtures. Quartz, alumina, pyrolytic boron nitride, glassy carbon, polycrystalline diamond film, porous graphite, and sapphire substrates were covered with a thin film of molten gallium and were exposed to a microwave plasma containing a range of gas phase species. During the plasma exposure, molten gallium flowed on all the substrates forming a thin film, which followed by formation of a thin polycrystalline film along with sparse nanowires. Gallium droplets were intentionally put on these polycrystalline oxide covered substrates and further synthesis experiments were carried out. The nanowires and other one-dimensional structures discussed in this paper were grown from

these large gallium drops. The substrate temperature was measured using an infrared pyrometer to be approximately 550°C for 700 W microwave power, 40 Torr total pressure, and 8.0 sccm O_2 in 100 sccm of hydrogen in the inlet stream. The experiments were performed at the following range of growth conditions: microwave power of 600-1200W, pressure of 30-60 Torr, growth duration of 1-12 hours, 0.6-10 sccm O_2 0-2 sccm CH_4 in 100 sccm of hydrogen in the feed gas. The post-synthesis samples were imaged using a LEO 1430 scanning electron microscope (SEM). As-grown samples were analyzed for crystalline quality using a Rigaku powder X-ray diffractometer (XRD). Individual nanowires were analyzed for crystallinity and composition using high-resolution transmission electron microscopy (HRTEM) (200kV JEOL 2010F) and Energy Dispersive X-ray spectroscopy (EDX). The samples for TEM analysis were prepared by scraping the nanowire mass from the substrate, dispersing in acetone and dropping on to a copper TEM grid.

Based on the average values of surface energies for gallium oxide (1.105 J/m^2 determined from heat of sublimation data and molten gallium (0.718 J/m^2, the contact angle is estimated as 180° using the equation of state and Young's equation. Poor wet-ability of gallium oxide with molten gallium was further confirmed by two different experimental observations. Molten gallium film spread on polycrystalline gallium oxide film was converted into droplets when exposed to microwave plasma containing oxygen and hydrogen radicals for less than ten minutes. The second experimental observation was the convex meniscus indicating obtuse contact angle between the gallium oxide rod and the molten gallium at the interface. In theory, other molten metals such as In, Al, Sn, and Zn would also form a convex meniscus with their oxides due to high surface energies.

As shown in Figures 1, 3, and 22, SEM images of multiple sub-micron thick and nanometer scale gallium oxide form needles grown

from a large gallium pool. In addition to nanoscale wires, well faceted one-dimensional structures thicker than 5 μm were also obtained as shown in Figure 8. The XRD (spectrum not shown) confirmed the as synthesized sample to be monoclinic gallium oxide phase (a_0 = 12.23Å, b_0 = 3.04Å, c_0 = 5.8Å, β=103.7 ., C2/m).

Figure 1 illustrates the bulk synthesis of one dimensional gallium oxide. Figures 1, 3, and 22 show sub-micron thick and nanometer scale gallium oxide rods. Figure 8 shows a well-faceted micron thick gallium oxide rods synthesized using a large gallium pool and microwave plasma containing atomic oxygen. In addition to the nanowires, nanostructures were obtained with paintbrush-like and tubular morphologies on the substrate stage around the substrate that was towards the edge of the dense plasma region.

As illustrated in Figures 12, 13, 16 and 23, the individual whiskers have tip diameters ranging from 10-100nm. Table 1 lists the experimental conditions under which different one-dimensional morphologies were obtained. In the current plasma reactor setup, a ball shaped plasma sits at the center of a circular substrate stage, which makes conditions (radical densities) to be different at different radial positions.

Figure 16 shows gallium oxide 1-D structures with interesting morphologies. Figure 12 shows a cluster of paintbrush-like one-dimensional structures of gallium oxide grown out of a gallium pool. Figure 13 depicts an individual gallium oxide nanopaintbrush. Figures 16 and 22 show micron scale gallium oxide tubes grown in the same experiment as the structures in Figures 12 and 13.

Table 1. Summary of experimental conditions versus the resulting one-dimensional structures.

Morphology	Flow rate of O_2 in 100 sccm of H_2 (sccm)	Microwave power (W)	Pressure (Torr)	Duration (Hr)	Location on the substrate
Nanoscale wires	0.6-10	600-900	30-50	1-12	On top of the micron to millimeter sized gallium droplets near the center of the substrate
Micron scale, well faceted rods	0.6-10	600-900	30 50	1 12	Clustered around the micron to millimeter sized gallium droplets
Nanopaintbrushes	7-10	600-1200	30-60	2-10	Near the edges of the substrate
Micron scale tubes	7-10	600-1200	30-60	2-10	Near the edges of the substrate

The EDX (spectrum not shown) confirmed that the individual nanowires consist of Ga (K_α at 9.3 keV, at 1.11 eV) and O (K_α at 0.53 keV). Figure 3A shows a bright field TEM image of a 100 nm thick nanowire. The HRTEM image in Figure 18 shows a 25 nm thick gallium oxide nanowire. The lattice spacing in HRTEM image also matched that for bulk beta-gallium oxide. The insert in Figure 18 shows the corresponding selected area electron diffraction pattern taken along the [001] zone axis.

The nanowire growth direction was determined to be [110]. Three nanowire samples were examined and the high-resolution TEM results were similar, i.e., structures were devoid of any stacking faults. The absence of stacking faults within the nanowire structures contradicts prior suggestions of structural defect mediated growth mechanisms for one-dimensional structures. For

example, in the case of diamond cubic materials, it was previously suggested that two or more parallel stacking faults are required to form a re-entrant corner for continuous kink creation and step propagation. Typically, the re-entrant corner mediation for growth of a crystal would not necessarily lead to one-dimensional structures. Thus, the present experimental results with nucleation and growth of multiple nanowires from molten gallium suggest a different nucleation and growth phenomenon.

Figures 18 and 23 illustrates TEM analysis of individual nanowires. Figure 23 shows bright field TEM image of an individual gallium oxide nanowire about 100 nm thick. Figure 18 shows a HRTEM image of a 25 nm thick nanowire. The insert shows a selected area electron diffraction pattern taken along the [001] zone axis. It is postulated that the nucleation and growth of oxide nanowires occurs in three basic steps: (1) dissolution of oxygenated gallium species into molten gallium; (2) phase segregation to create multiple nuclei on the surface; and (3) homo-epitaxial growth of nuclei into one-dimensional structures from the bottom using the dissolved species. The surface dynamics of nuclei on molten gallium, i.e., pattern formation and the time of coalescence determine if the resulting nanostructure would be a nanowire, tube, or nanopaintbrush.

As depicted in the schematic in Figure 20, the rapid dissolution process results in the spontaneous nucleation of nanometer-scale metal oxide nuclei on the surface. More particularly, as shown in the schematic in Figure 21, the rapid dissolution process results in the spontaneous nucleation of nanometer-scale gallium oxide nuclei on the surface. These surface-segregated nuclei in the absence of re-dissolution could coalesce on the surface to form a crust. The crust formation prevents further growth of nanometer-scale nuclei in one-dimension and leads to thick, polycrystalline film over molten gallium. Due to poor wetability of gallium oxide with gallium, the gallium oxide nuclei

surface out but do not propagate laterally thus ensuring growth in one dimension perpendicular to the molten gallium surface. In the case of hexagonal nuclei formation, lateral growth is probably unavoidable, as these nuclei would propagate parallel to the molten gallium surface thus eliminating the possibility of growing into a nanowire. This has been observed with plasma nitridation of bulk pools of molten gallium using pure nitrogen environments at substrate temperature of 800°C or greater. In this case, nitrogen plasma exposure resulted in hexagonal, platelet shaped GaN crystals forming a crust over the molten gallium surface. The resulting crust was found to be highly c-plane textured with in-plane orientation between crystals. However, the plasma nitridation of thin gallium films resulted in the growth of gallium nitride nanowires due to the deprived supply of gallium necessary for lateral growth of platelet shaped crystals. In the present work, hydrogen/oxygen chemistry seems to provide simultaneous dissociation of surface-segregated oxide nuclei to prevent complete crust formation enabling one-dimensional growth.

In Figure 20 and 21, the schematic depicts possible growth routes for multiple nanowires, tubes, and nanopaintbrushes out of a large metal pool, for example a gallium pool. The proposed three-step mechanism is further analyzed using thermodynamic arguments and a specific set of experiments. The Gibbs free energies for reactions between both molecular and atomic oxygen species with molten gallium to produce solid gallium oxide are determined to be highly negative, which suggests spontaneity. The estimated nuclei size of gallium oxide nucleation out of molten gallium using classical nucleation theory is predicted to be in the nanometer scale for extremely low partial pressures of oxygen in the vapor phase over molten gallium. This suggests that bulk nucleation of nanometer scale gallium oxide nuclei using oxygen vapor over a molten gallium pool is thermodynamically feasible. The main question is however, whether the molten gallium vapor phase

interaction results in dissolution or in generation of vapor phase species such as gallium sub-oxides, gallium hydrides, and pure gallium vapor. The generation of vapor phase species would lead to eventual loss of gallium from the experiments. In any case, the overall interaction of monoatomic oxygen with molten gallium is represented with the following set of reactions. Surface species are denoted with star superscripts.

$$Ga_{(l)} + O_{(g)} \Leftrightarrow GaO(g) \quad (1)$$

$$2Ga_{(l)} + O(g) \Leftrightarrow Ga_2O(g) \quad (2)$$

$$Ga_{(l)} + O(g) \Leftrightarrow GaO^* \quad (3)$$

$$2Ga_{(l)} + O(g) \Leftrightarrow Ga2O^* \quad (4)$$

The surface sub-oxide species from (3) and (4) could undergo dissolution to produce sub-surface species and recombination to remove the dissolved oxygen from molten gallium according to:

$$Ga2O^* \Leftrightarrow Ga_2O_{(l)} \quad (5)$$

$$2Ga_2O_{(l)} \Leftrightarrow 4Ga(l) + O2(g) \quad (6)$$

Reactions 3 and 4 represent chemisorption of oxygen on molten gallium surface, and Reactions 5 and 6 represent dissolution of surface species into the bulk and bubbling in gallium pools upon exposure to the plasma, respectively. The diffusion of chemisorbed oxygen complexes versus the thermal desorption determines the solubility of dissolved oxygenated species within molten gallium. The surface diffusion coefficient is typically orders of magnitude higher than the bulk diffusion coefficient. The average lifetime of a surface adsorbed species is a function of the absolute value of the heat of desorption and temperature. At 600 K, the average lifetime of a chemisorbed species such as Ga_2O^* on the molten gallium surface is estimated to be on the order of 1 second, which is two and five orders of magnitude greater than the characteristic time scales involved with bulk and surface diffusion processes,

respectively. A characteristic length scale of 1 μm was assumed. Thus, the surface adsorbed species are much more likely to undergo diffusion processes, bulk or surface, than desorption into the vapor phase. Reactions 1 and 2 represent abstraction of gallium using atomic oxygen to produce vapor phase species and represent continuous loss of gallium metal. A set of experiments was performed to track the mass loss of gallium in the experiments with exposure to a plasma containing only oxygen. After several hours of exposure to oxygen plasma, a thin crust was seen on top of the gallium pool with only a negligible change in weight. Complete conversion of gallium to solid gallium oxide would cause a weight increase of approximately 34%. The experimental results showed nominal net loss of mass indicating that oxygen interaction with molten gallium occurs via a dissolution process much more significantly than chemical vapor transport of gallium using oxide complexes. The thin crust formation and occasional observations of nanowire growth using direct oxygen plasma indicates that hydrogen plays a significant role in preventing crust formation by causing reduction of oxide nuclei to gallium metal. Accordingly, two sets of experiments were performed to observe the interaction of hydrogen plasma with solid gallium oxide and molten gallium. The overall reactions for gallium oxide dissociation are represented in Reactions 7 and 8. Both of these reactions could easily be achieved with either molecular or atomic hydrogen.

$$Ga_2O_{3(s)} + 4H_{(g)} \Leftrightarrow Ga_2O_{(g)} + 2H_2O \quad (7)$$

$$Ga_2O_{3(s)} + 6H_{(g)} \Leftrightarrow 2Ga_{(l)} + 3H_2O \quad (8)$$

The above reactions also compete with the following reactions:

$$Ga_{(l)} + H \Leftrightarrow GaH_{(g)} \quad (9)$$

$$Ga_{(l)} + H \Leftrightarrow GaH^* \quad (10)$$

$$GaH^* \Leftrightarrow GaH_{(l)} \quad (11)$$

$$2GaH_{(l)} \Leftrightarrow 4Ga_{(l)} + H_{2(g)} \quad (12)$$

$$H_{(g)} + H_{(g)} \Leftrightarrow H_2 \quad (13)$$

The above set of reactions was examined by performing experiments involving hydrogen plasma exposure of molten gallium and solid gallium oxide in separate runs. After several hours of exposure to hydrogen plasma, the gallium oxide solid phase reverted to metallic gallium with a minimal decrease in the total weight. Over different durations of exposure, the mass loss of molten gallium was within ten percent of the starting molten gallium mass. This loss in mass is much more than the theoretically estimated weight loss due to gallium vaporization at the exposure temperatures and pressures. However, the experimentally observed mass loss is much less than the expected mass loss estimated using typical values of gallium abstraction probabilities with hydrogen and the typical process parameters in the flow reactor. Using similar abstraction probability values for both hydrogen and

oxygen, the mass loss of gallium via abstraction process is estimated to occur at linear rates on the order of tens of milligrams per hour. However, a constant mass loss of less than 10 mg was observed over total period of 12-hour exposure to hydrogen plasma. In addition, bubbling of molten gallium was observed during microwave plasma treatment. These results indicate that the interaction of monoatomic hydrogen with molten gallium occurs with chemisorption followed by dissolution of hydrides as indicated by reactions 11, 12, and 13. These observations support the hypothesis that hydrogen is responsible for promoting oxide nanowire growth by etching surface-segregated solid gallium oxide nuclei, thus inhibiting the lateral growth of surface nuclei by agglomeration.

The subsequent growth of surface nuclei could occur through attachment kinetics with the sub-oxide species in the dissolved phase or with gas phase species. However, the observation of minimal loss in the mass of the solid gallium oxide phase upon exposure to hydrogen plasma indicates that the generation of vapor phase gallium sub-oxide species is negligible. This is in contradiction with previously suggested mechanisms for oxide nanowire growth using carbothermal or high temperature reduction. The nanometer scale wires showed insignificant tapering from bottom to top, indicating that growth via basal attachment of growth species is more likely than attachment at the tip or at the nanowire perimeter. Micron-thick wires clearly exhibited tapering only for short lengths from the top and exhibited faceting at the tips, clearly indicating significant etching at the tip of the micron scale rods.

As shown in the schematic in Figure 21, growth of tubes and paintbrushes can be explained based on initial nucleation and nuclei movement on the molten gallium surface. In some instances, the use of hydrogen in the microwave plasma allowed agglomeration of nanometer scale surface nuclei into either solid or annular

hexagonal patterns. Subsequent attachment of the growth species to solid and annular patterns results in the growth of micron thick hexagonal cross-section solid rods and hexagonal cross-section tubular structures, respectively. Presently, the reason for hexagonal pattern formation is not clear. In the case of agglomeration of neighboring nanometer scale nuclei at an intermediate stage, the structure evolves into paintbrush morphology. This type of agglomeration could occur due to intermittent changes in the gas phase and temperature that are inherent towards the edge of the plasma discharge. Sequential experiments were performed with the synthesis of nanopaintbrushes and tubular structures. It was observed that upon extended exposure to the plasma, the one-dimensional structures shown in Figures 12 and 16 converted to nanometer scale wires shown in Figures 3 and 22. In some instances, the extended exposure to hydrogen/oxygen plasma, the oxide nanostructures developed branching indicating that secondary nucleation occurred following the hydrogen etching of oxide in the tip region to gallium metal. The current efforts are focused on determining the agglomeration dynamics of nuclei on molten gallium surface, necessary to control the morphology of resulting nanostructures.

Apart from Ga/Ga_2O_3, it is anticipated that this direct synthesis technique could be extended to oxide nanostructures of other low melting metallic systems. As shown in Table 2, extremely low partial pressures of molecular and atomic oxygen are sufficient thermodynamically for creating nanometer scale nuclei for a variety of other low melting metallic systems such as Al/A_2O_3, In/In_2O_3, Sn/SnO_2 and Zn/ZnO. Theoretical estimations of contact angles for these metal oxides with respective molten metals illustrate poor wetting characteristics. Thus, the direct synthesis of nanostructures using appropriate hydrogen/oxygen gas phase chemistry should be applicable to other important metal-oxide systems.

Table 2. Minimum partial pressures of monoatomic and diatomic oxygen required for 1 nm sized nuclei of the respective oxides at 1000K. Thermodynamic properties were obtained from ref 36. The estimated Gibbs free energy values for overall reactions are indicated in square brackets.

Metal	Overall formation reaction using atomic oxygen	Overall formation reaction using Molecular oxygen	Minimum partial pressure of O required (Torr)	Minimum partial pressure of O_2 required (Torr)
Ga	$2Ga_{(l)} + 3O_{(g)} \rightarrow Ga_2O_{3(s)}$ [$\Delta G^0 = -1326.2$ kJ/mol]	$2Ga_{(l)} + 3/2O_{2(g)} \rightarrow Ga_2O_{3(s)}$ [$\Delta G^0 = -763.1$ kJ/mol]	4×10^{-18}	9×10^{-19}
In	$2In_{(l)} + 3O_{(g)} \rightarrow In_2O_{3(s)}$ [$\Delta G^0 = -1169.2$ kJ/mol]	$2In_{(l)} + 3/2O_{2(g)} \rightarrow In_2O_{3(s)}$ [$\Delta G^0 = -606.1$ kJ/mol]	2×10^{-16}	2×10^{-15}
Al	$2Al_{(l)} + 3O_{(g)} \rightarrow Al_2O_{3(s)}$ [$\Delta G^0 = -1925.2$ kJ/mol]	$2Al_{(l)} + 3/2O_{2(g)} \rightarrow Al_2O_{3(s)}$ [$\Delta G^0 = -1362.1$ kJ/mol]	6×10^{-26}	2×10^{-34}
Sn	$Sn_{(l)} + 2O_{(g)} \rightarrow SnO_{2(s)}$ [$\Delta G^0 = -748.2$ kJ/mol]	$Sn_{(l)} + O_{2(g)} \rightarrow SnO_{2(s)}$ [$\Delta G^0 = -372.8$ kJ/mol]	4×10^{-13}	8×10^{-9}
Zn	$Zn_{(l)} + O_{(g)} \rightarrow ZnO_{(s)}$ [$\Delta G^0 = -435.9$ kJ/mol]	$Zn_{(l)} + 1/2O_{2(g)} \rightarrow ZnO_{(s)}$ [$\Delta G^0 = -248.3$ kJ/mol]	2×10^{-14}	2×10^{-11}

The present invention provides a method of synthesizing bulk amounts of highly crystalline gallium oxide tubes, nanowires, and nanopaintbrushes using large gallium pools and a microwave plasma containing atomic oxygen. Direct use of gallium melts in plasma environments allowed bulk synthesis with high nucleation densities and allowed for template-free synthesis of nanostructures with

unique geometries. Plasma excitation of gas phase allowed for synthesis of single crystal quality nanostructures at much lower temperatures than commonly reported. In addition, the control of gas phase chemistry allowed the manipulation of the nanostructure composition and morphology. Demonstration of this technique with gallium oxide presents a new route for synthesizing important metal oxides such as indium oxide, tin oxide, and zinc oxide directly using the respective metals.

The foregoing detailed description is given primarily for clearness of understanding and no unnecessary limitations are to be understood therefrom, for modification will become obvious to those skilled in the art upon reading this disclosure and may be made upon departing from the spirit of the invention and scope of the appended claims. Accordingly, this invention is not intended to be limited by the specific exemplifications presented hereinabove. Rather, what is intended to be covered is within the spirit and scope of the appended claims.